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Halide-hydrogen vapor transport for growth of ZnO single crystals with controllable electrical parameters

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ABSTRACT

The advantages of $HCl+H_2$ gas mixture as a chemical vapor transport agent for ZnO single crystals growth in the closed growth chambers are shown in comparison with Cl_2, HCl and H_2 by the thermodynamic analysis. The influence of the growth temperature, density of $HCl+H_2$ transport agent and undercooling were investigated experimentally on the rate of ZnO mass transport. It was shown that $HCl+H_2$ gas mixture provides (i) a rather high growth rate (up to 1 mm per day), (ii) a minimization of wall adhesion effect and deformations during a post-growth cooling, (iii) stable and reproduced seeded growth of the void-free single crystals with controllable conductivity and charge carrier concentration varied in the range of 2–22 $(\Omega\,\mathrm{cm})^{-1}$ and $(1–31)\cdot 10^{17}\,\mathrm{cm}^{-3}$, respectively. The characterization by the photoluminescence spectra, the transmission spectra and the electrical properties, as well as energy spectra of stable Cl-containing defects are analyzed.

1. Introduction

Zinc oxide (ZnO) crystals have recently drawn attention due to a relatively low-price and to their application perspectives in optoelectronics [1]. Commercially available crystals and substrates are usually obtained by hydrothermal methods [1,2]. However, the corresponding equipment is expensive and the possible contamination with mobile Li or K ions limiting ZnO utilization in electronics [1] causes necessity of the special adjustments of critical growth conditions [3].

The application of halides, in particular HCl, as a chemical vapor transport agent (TA), which effectively react with ZnO and can provide a dense medium of chemical interaction products, might be a cheaper and simpler growth method based on the chemical vapor transport in sealed chambers. Moreover, it can be also the perspective for obtaining materials homogeneously doped in the growth process, as many metals (including magnetic impurities, as well as acceptors for insulator substrates) characterized by a rather low vapor pressure usually effectively interact with HCl by creating easily flying and stable chloride compounds. This can become viable for solid solution crystals based on ZnO, as it was recently demonstrated for obtaining ZnCdS:HCl single crystals [4].

The recent viable direction of wide band-gap II–VI semiconductor compounds application is the fabrication of nanoporous matrices (NM) (nanotemplates), which give the possibility of obtaining nanowires and nanotubes of various materials as promising structures for optoelectronics. The easiest and most cost-effective method to obtain NM is electro-chemical etching (ECE), which, however, can be efficiently used only on the homogeneously doped substrates with controlled high conductive properties [4–7]. The increase in the substrate conductivity provides the decrease in the diameter of pores. The possible application of ZnO substrates for manufacturing NM sets the background for development of control and stabilization of their electrical properties.

The use of H_2 as a TA gives the possibility to grow large ZnO crystals. However, in some cases, these crystals are characterized by structural defects such as angle boundaries and voids [8]. Furthermore, a strong mechanical contact between crystals and walls of quartz growth chambers leads to a partial destruction of crystals during a post-growth cooling. Using HI and HBr as a TA has not allowed reaching the high growth rate of bulk crystals [9]. The utilization of Cl_2 as a TA for ZnO did not provide positive results [10]. The effect of $HgCl_2$, NH_4Cl and $ZnCl_2+H_2O$ halides was also reported [9,11,12]. The corresponding results showed a low rate of the ZnO mass transport. The unseeded growth method allowed obtaining thin prismatic or needle-form crystals [9,11]. At the same time, according to research data, the possibility of growth of large ZnO single crystals having a high structural perfection using chlorine halides was not systematically analyzed. The given investigation addresses this issue.

The exact structure of the centers containing Cl impurity in ZnO crystals and their activation energy are still poorly studied, and the

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